Control of the SO_2 Coordination Mode at the (Monochelate)rhodium Complex ClRh(P~O)(P⌒O) with the Hemilabile Ligand $Cy_2PCH_2CH_2OCH_3$☆

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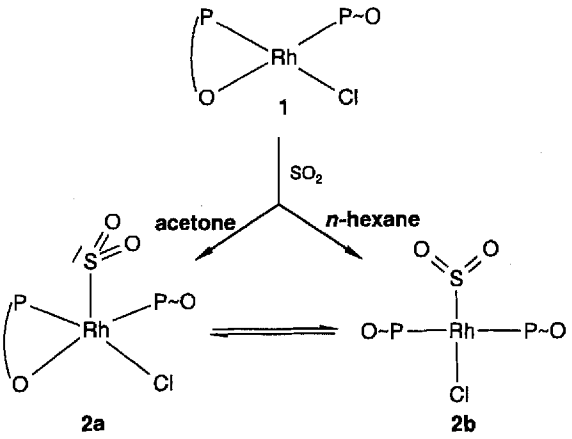
The SO_2 coordination mode at the rhodium complex [ClRh(P~O)(P⌒O)] (**1**) [P⌒O = η^2(*O,P*)-chelated $Cy_2PCH_2CH_2OCH_3$ ligand; P~O = η^1(*P*)-coordinated] is controlled by the hemilabile ligand $Cy_2PCH_2CH_2OCH_3$ and shows a dependence on the polarity of the solvent. In polar organic solvents (e.g. acetone) the addition of sulfur dioxide results in the formation of a trigonal-pyramidal oriented SO_2 group in [ClRh(η^1-SO_2)(P~O)(P⌒O)] (**2a**). However, in nonpolar media (e.g. *n*-hexane) a trigonal-coplanar geometry of the SO_2 unit in [ClRh(η^1-SO_2)(P~O)$_2$] (**2b**) is favored.

Because of its property to function as a Lewis acid or a Lewis base sulfur dioxide is able to bind to transition metals in different ways. The η^1(*S*)-coplanar and η^1(*S*)-pyramidal addition of this molecule to metal centers as well as the η^2-coordination via sulfur and oxygen are the most important structural types which were investigated in detail[1]. From energetic studies of the frontier orbitals of rhodium and iridium compounds a dependence of the coordinative behavior of sulfur dioxide on the kind of the complex fragment is observed. Whereas d^8-ML_3 units prefer a trigonal-planar M–SO_2 arrangement[2], a trigonal-pyramidal M–SO_2 geometry is energetically favored in the case of a d^8-ML_4 building block[3]. While [ClMSO$_2$(PR$_3$)$_2$] complexes (M = Rh, Ir; R = *i*Pr, Cy)[2,4] belong to the first category the Vaska analogous species [ClIrSO$_2$(PR$_3$)$_2$CO] (R = Ph, *i*Pr, Cy)[5] are among the second classification. In not a single case have both coordination modes (trigonal-planar and trigonal-pyramidal) at one complex and reversible transformation of both isomers into each other been realized so far. We now observed that the use of the hemilabile ether-phosphane ligand $Cy_2PCH_2CH_2OCH_3$ enables a controlled SO_2 coordination to the mono(chelate)rhodium complex [ClRh(P~O)(P⌒O)][6] (**1**) [P⌒O = η^2(*O,P*)-chelated $Cy_2PCH_2CH_2OCH_3$ ligand; P~O = η^1(*P*)-coordinated] due to the polarity of the solvent.

In polar organic solvents like acetone, favoring a (polar) rhodium-oxygen contact, sulfur dioxide behaves as a Lewis acid. Accordingly, SO_2 is added to this d^8-RhL_4 fragment with retention of the *O,P*-chelate in **1** in such a fashion that a trigonal-pyramidal Rh–SO_2 structure results (Scheme 1). In contrast, nonpolar media like *n*-hexane destabilize the rhodium-oxygen bond in **1** with formation of a d^8-RhL_3 unit to which sulfur dioxide is added as a Lewis base. Thereby in [ClRhSO$_2$(P~O)$_2$] (**2b**) SO_2 is oriented in a η^1-coplanar manner (Scheme 1). The isomeric complexes **2a** and **2b** cannot be obtained only by a controlled synthesis. Moreover, they can even be transformed into each other by solvents with different polarity. If acetone is removed from a solution of **2a** and exchanged for *n*-hexane, complex **2b** is generated quantitatively with a color change from yellow to brown. Conversely, **2b** is likewise completely transformed into **2a** upon exchange of *n*-hexane for acetone. In dichloromethane the polarity of which is intermediate between that of acetone and that of *n*-hexane, an additional dependence of the SO_2 coordination type on temperature is observed. At −40 °C only the signals of isomer **2a** are displayed in the $^{31}P\{^1H\}$-NMR spectrum. As the temperature of a CH_2Cl_2 solution of **2a** is raised to room temperature, along with the ^{31}P resonances of **2a** also those of isomer **2b** are observed. A quantitative transformation **2a** → **2b** does not occur in this solvent.

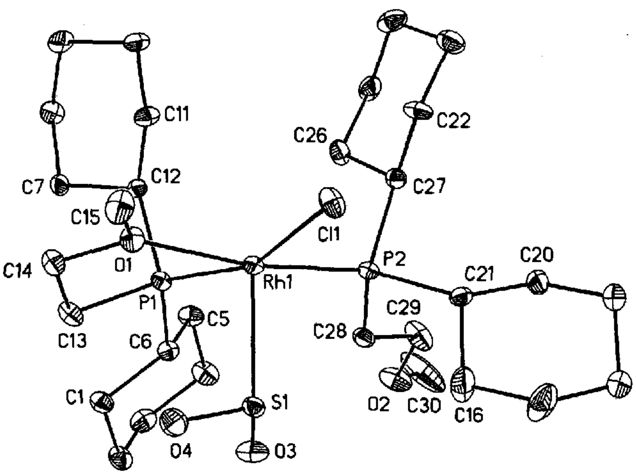
Scheme 1



In both isomers **2a** and **2b** the coordination of SO_2 to the rhodium center is so strong, that at least in vacuo at room temperature no Rh–S bond cleavage takes place. In agreement with this observation **2a** and **2b** are not oxidized by dioxygen to the corresponding sulfato complexes. The complexes **2a** and **2b** were characterized on the basis of their IR and $^{31}P\{^1H\}$-NMR spectra. In addition, their reversible isomerization was followed $^{31}P\{^1H\}$-NMR spectroscopically. The respective bonding mode of sulfur dioxide was disclosed by the different absorptions of the SO_2 stretching vibrations in the IR spectrum[1a] which appear clearly at higher frequencies in the case of a trigonal-planar $M-SO_2$ unit. While the AB part of an ABX spin system was established in the $^{31}P\{^1H\}$-NMR spectrum of **2a** ([D$_6$]acetone), a doublet appears in the spectrum of **2b** (C_6D_6) for the equivalent phosphane P atoms.

The η^1(*S*)-pyramidal coordination geometry of the SO_2 unit in **2a** was confirmed by an X-ray structural analysis (Figure 1). The ligands are arranged almost square-pyramidal about the rhodium center with sulfur dioxide in the apical position of the pyramid.

Figure 1. ORTEP plot of the crystal structure of **2a**. Selected bond lengths [Å] and angles [°]: Rh(1)–P(1) 2.281(2), Rh(1)–P(2) 2.281(2), Rh(1)–Cl(1) 2.391(2), Rh(1)–O(1) 2.238(5), Rh(1)–S(1) 2.340(2), S(1)–O(3) 1.456(5), S(1)–O(4) 1.474(5); P(1)–Rh(1)–P(2) 102.64(7), O(1)–Rh(1)–P(1) 78.54(14), P(1)–Rh(1)–S(1) 93.55(7), O(3)–S(1)–O(4) 111.3(3)



The distance of the rhodium atom above the approximate plane formed by the four basal donor functions is 0.238 Å. In consonance with the stability and inertness of **2a** toward oxidation, the Rh–S distance [2.340(2) Å] is short for a trigonal-pyramidal bound SO_2 group[7]. The normal angle between the Rh–S vector and the resultant of the S–O vectors of 121(6)° is close to the range usually reported for a trigonal-pyramidal SO_2 geometry[7].

The complexes **2a** and **2b** are the first examples of a reversible transformation of a trigonal-planarly coordinated SO_2 unit into a trigonal-pyramidal geometry being controlled by a hemilabile ligand. This isomerization is triggered by the different polarity of the solvent. However, this isomerization process is rendered possible by the special ability of ether-phosphane ligands to form weak rhodium-oxygen contacts, which can be easily cleaved again.

Sulfur dioxide complexes with "classical" phosphane ligands, the P donors of which create a stable bond with the metal center, are therefore characterized by their SO_2 geometry. Hence, a transformation of the SO_2 coordination mode in those cases can only be achieved by a chemical reaction which changes the complex fragment[5].

Besides the alkyl migration in cationic rhodium complexes[8] which is controlled by the basicity of ether-phosphanes, the presented influence on the SO_2 coordination mode is a further illustrative example of the ability of this type of ligands to act as controlling ligands in organometallic model reactions.

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Experimental

All manipulations were carried out under argon by use of standard Schlenk techniques. – Solvents were dried with appropriate reagents and stored under argon. – Elemental analyses: Carlo Erba 1106. – AAS: Perkin-Elmer model 4000. – FD-MS: Finnigan MAT 711A (8 kV) modified by AMD. – FAB-MS: Finnigan MAT TSQ 70 (10 kV, 50°C). – IR: Bruker IFS 48 FT-IR. – ^{31}P, ^{13}C, and ^{103}Rh NMR: Bruker DRX 250 spectrometer at 101.25, 62.90, and 7.9 MHz. ^{13}C chemical shifts were measured relative to deuterated solvent peaks, which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 ($\delta = 0$). The ^{103}Rh-NMR resonances were measured by using a 2D (^{31}P,^{103}Rh)$\{^1H\}$ experiment[9]. – Chemical shift values are referred to $\Xi(Rh) = 3.16$ MHz[10]. – The starting compounds $Cy_2PCH_2CH_2OCH_3$[11] and $[ClRh(P{\sim}O)(\overset{\frown}{PO})]$[6] (**1**) were prepared as previously described.

Chloro[dicyclohexyl(2-methoxyethyl)phosphane-P][dicyclohexyl(2-methoxyethyl)phosphane-O,P](η^1-sulfur dioxide-S)-rhodium(I) (**2a**): Sulfur dioxide was bubbled through a solution of **1** (65 mg, 0.1 mmol) in 5 ml of dichloromethane at −40°C. A spontaneous color change from orange to brown occurred. Excess sulfur dioxide was removed in vacuo. A pale yellow solid precipitated by cooling the solution to −70°C. The supernatant layer was decanted and the remainder washed with 10 ml of *n*-hexane. The solid was dried in vacuo. Yield 71 mg (89%) of **2a**, yellow solid, m.p. 67°C (dec.). – IR (KBr): $\tilde{\nu} = 1152$ cm^{-1}, 1019 (SO_2), 1107, 1073 (C_2O). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40°C): $\delta = 62.9$ (dd, $^1J_{RhP} = 155.4$, $^2J_{PP} = 30.2$ Hz, η^2(*O,P*)-chelated $Cy_2PCH_2CH_2OCH_3$), 38.6 (dd, $^1J_{RhP} = 176.2$, $^2J_{PP} = 30.2$ Hz, η^1(*P*)-coordinated $Cy_2PCH_2CH_2OCH_3$). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40°C): $\delta = 74.2$, 69.8 (s, CH_2O), 62.0, 58.5 (s, OCH_3), 36.8 (m, PCH), 30.7–26.4 (m, C_6H_{11}), 22.4 (m, PCH_2). – ^{103}Rh NMR (CD_2Cl_2, 22°C): $\delta = 1650$. – MS (FD, 35°C), *m/z*: 650.1 [$M^+ - SO_2$]. – $C_{31}H_{60}Cl_3O_4P_2RhS$ (800.1), **2a** · CH_2Cl_2: calcd. C 46.54, H 7.56, Cl 13.29, Rh 12.86, S 4.01; found C 46.73, H 7.82, Cl 13.53, Rh 12.59, S 4.38.

Chlorobis[dicyclohexyl(2-methoxyethyl)phosphane-P](η^1-sulfur dioxide-S)rhodium(I) (**2b**): Sulfur dioxide was bubbled through a solution of **1** (65 mg, 0.1 mmol) in 20 ml of *n*-hexane at 0°C until a dark brown solution was obtained. The reaction takes place within approximately 2 min. The solution was evacuated to remove excess sulfur dioxide. A yellow solid precipitated by cooling the solution to −70°C. The supernatant layer was decanted and the remainder washed with 10 ml of *n*-hexane at −70°C. The solid was dried in vacuo. Yield 62 mg (86%) of **2b**, yellow solid, m.p. 86°C (dec.). – IR (KBr): $\tilde{\nu} = 1255$ cm^{-1}, 1152 (SO_2), 1105 (C_2O). – $^{31}P\{^1H\}$ NMR (C_6D_6, 22°C): $\delta = 30.2$ (d, $^1J_{RhP} = 109.4$ Hz, η^1(*P*)-coordinated $Cy_2PCH_2CH_2OCH_3$). – $^{13}C\{^1H\}$ NMR (C_6D_6, 22°C): $\delta = 70.2$ (s, CH_2O), 58.4 (s, OCH_3), 35.4 (vt, $N = 24$ Hz[12], PCH), 30.8–26.8 (m, C_6H_{11}), 20.9 (vt, $N = 14$ Hz[12], PCH_2). – ^{103}Rh NMR (CD_2Cl_2, 22°C): $\delta = 955$. – MS (FAB, 50°C), *m/z*: 650.1 ($M^+ - SO_2$). – $C_{30}H_{58}ClO_4P_2RhS$ (715.15): calcd. C 50.39, H 8.17, Cl 4.96, Rh 14.39, S 4.56; found C 48.76[13], H 8.02, Cl 4.60, Rh 14.17, S 4.84.

X-ray Structural Analysis of **2a**: Single crystals were obtained from a CH_2Cl_2 solution at −30 °C. $C_{33}H_{64}Cl_7O_4P_2RhS$, $M = 969.95$, orthorhombic space group *Pbca*, $a = 12.662(3)$, $b = 16.556(4)$, $c = 41.895(9)$ Å, $d_{\text{calcd.}} = 1.467$ g/cm^3, $\mu(\text{Mo-}K_\alpha) = 0.969$ mm^{-1}, $2\Theta = 4-50°$, $V = 8783(4)$ Å^3, $Z = 8$, measured reflexions = 14099, observed reflections = 7724, observed reflections $(I \geqslant 2\sigma I) = 2918$, number of parameters = 434, $S = 1.012$, $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.044$, $wR2 = [\Sigma(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2} = 0.078$. A crystal with the dimensions 0.20 × 0.20 × 0.40 mm was mounted on a glass fiber and transferred to a P4 Siemens diffractometer (graphite-monochromated Mo-K_α radiation). The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The structure was solved by the Patterson method[14] and refined by the least-squares method (based on F^2) with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). An absorption correction ψ scan was applied. Max. and min. transmission are 0.783 and 0.656, respectively. Maximum and minimum peaks in the final difference synthesis were 0.491 and −0.458 eÅ^{-3}. Three CH_2Cl_2 molecules were found in the asymmetric unit. – Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405241, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Michael Hanack* on the occasion of his 65th birthday.

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